

its productivity now has a year round assured supply of water and the farmers in the area grow seasonal crops throughout the year. Rice, Wheat, Sugar-cane, Groundnuts and Onion are some of the crops cultivated.

Furthermore, over the past seven years, no build up of salts in the soil has been observed through the use of treated effluent. Improved yields over former years as may be seen from Table-II also go to prove that the residual lignins, polysaccharides, etc. in the effluent are beneficial to plant growth.

Finally percolation of the effluent through the soil further reduces the B.O.D. through the anaerobic decomposition of the organic matter. The soil acts as a filter media also, and removes part of the colour from the effluent.

#### SLUDGE DEWATERING & DISPOSAL

About 15 tonnes of settled solids are pumped out every day from the primary thickener. This sludge is at 5% consistency, and is dewatered in filtration

cum drying beds which are square pits containing filter media. Dewatering takes 24 hours and the dewatered sludge has a solids content of 13 to 15%. The sludge which has a calorific value close to that of ligneous coal is then used as a domestic fuel, land fill, and after digestion as a manure. Trials are now being conducted on the digestion of the sludge for the production of bio gas.

#### CONCLUSION

In conclusion it can be stated that not only has pollution been averted, but the success in the use of effluent for irrigation has turned otherwise fallow land productive. Furthermore, the water drawn from the river is used twice over, once in the service of industry and then later returned to the land for irrigation, thereby maintaining productivity while meeting our social commitments.

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## A Laboratory Study of Mini Lime Treatment of Dissolving Pulp Mill Coloured Effluent

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#### SUMMARY

In the Pulp Mill, Washing, Bleaching and Recovery Departments exert maximum colour, hence segregation has been recommended.

On treatment with lime alongwith lime mud there was observed 79% of colour removal and C.O.D. reduction to the tune of 51%. The overflow of lime treated effluent on reacting with Chlorine further improvement in colour takes place (89-93%). The Calcium value from the sludge produced during effluent treatment could be recovered by calcining.

#### INTRODUCTION

Though the present effluent regulation do not specify the colour of the Pulp mill effluent discharged, it concerns an Industry because it is a visible indicator of pollution, to the layman. This problem is enhanced where waste receiving stream governs domestic importance. Therefore, there is no way out but to treat the effluent to remove the colour.

The major sources of water pollution in the rayon grade pulp mill are prehydrolysis, washing, screening, bleaching and chemical recovery. These tend to discharge various quantities and types of pollutants. Pollutants discharged can be reduced using known pollution treatment techniques and operating efficiently the existing plants and machines. A major factor in this respect in the reduction of the overloading of existing plants. Overloaded plant or mill components often discharge continuously considerable quantities of pollutions. Hence in-plant control is a must before treatment procedure is undertaken.

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## SOURCES OF COLOUR IN THE PULP MILL EFFLUENT

Degradation products of lignins, tannins, and minor quantities of dyestuffs are prevalent chemical constituents to provide colour to effluents originating from Washing, Bleaching, Alkali extractions and Recovery sections of the Pulp Mill. As tannins are water soluble which in principle are removed in the prehydrolysis stage whereas microquantities of dyestuffs may not impart high colour. Therefore, considerable colour load contribution is from lignin based products.

As such native lignin is mostly light coloured. It has been shown that by the action of alkali on lignins, phenolic arylpropene moieties are converted to a great extent into quinonemethide structures. These reactive intermediates subsequently undergo transformation to yield conjugated structures such as substituted stilbene and arylcoumaran (<sup>1</sup>). Organic sulphides are also formed by the nucleophilic addition of sulphide ions with quinonemethide structures. In addition to these several other organic complex molecules derived from resins can also cause high colour in the effluent and these are produced during sulphate cooking.

There are several reports in the literature (<sup>2</sup>) regarding colour removal from pulp mill effluent. The excellent review by Mr. P.V.R. Subramaniam (<sup>3</sup>) gives a good account of decolourisation of Pulp Mill effluent. It has been pointed out that colour removal adopting a conventional biological treatment process is not significant (<sup>4,5</sup>) as it is very slow. At present coagulation process is faster and the only economically feasible method for effluent colour removal. Although there are number of claims about the potentiality of several coagulants (<sup>2</sup>), the most popular one is lime, may be because lime is cheap and readily available, also works well (<sup>6</sup>). It is more true where lime kiln is an integrated part of the Pulp Mill, as it provides the possibility of sludge recycling resulting in the recovery of chemical value thereby avoiding sludge disposal difficulty. However, salts of  $Fe^{2+}$  or  $Al^{3+}$  can work efficiently in combination with lower dosage of lime or as such in reducing the colour of effluent (<sup>6</sup>) if sludge handling and disposal does not pose problem as recovery of chemical value from such sludge is difficult.

### PRESENT WORK

With this knowledge, a major objective of this project, namely, coagulation of coloured bodies from rayon pulp mill effluent using lime as a coagulant and calcium carbonate as a flocculator has been achieved. The precipitation of coloured organic bodies in presence of lime is based on the relatively low solubility of calcium salts. However, the degree of precipitation does vary with the nature of the

effluent (which is dependent on the pulping process) and the quantity of lime used.

At the Gwalior Rayons (Mavoor) Pulp Mill the production of 180 tonnes of rayon grade pulp per day is based on raw material such as Bamboo, Eucalyptus, and firewoods. The process involves prehydrolysed sulphate cooking followed by CEHEDH Bleaching sequence. The water required for the process is drawn from the Chaliyar River flowing by the side of the factory. The process water (effluent) is discharged 1.6 KM/ 7 KM downstream of the factory. The river merges with the Arabian Sea 22 KM downstream of the factory.

Attached Table-I gives general characteristics of wastes of different origins of the Pulp Mill.

Quantitative study of different drains of the Gwalior Rayons (Mavoor) Pulp Mill reveal that, washing backwater, bleaching first alkali extraction backwater and evaporators drain exert maximum colour. Therefore, these drains need special attention with respect to decolourisation, hence a separate treatment is recommended. Therefore segregation of these highly coloured drains from rest of the mill effluent helps in reducing chemical consumption during treatment process as well as bulk handling problems.

After careful examination of these three drains individually, we learnt that effluent from washing and evaporators respond quickly (precipitation of colour) even to a small dose of lime (500 mg/l.), whereas bleaching first alkali extraction effluent needs higher dosage of lime (2,000 mg/l.) to achieve similar results. However, combination of these three drains do respond well to 1000 mg. of lime and 30,000 mg. of lime mud (50% dry content lime mud obtained from lime kiln recovery system) per litre of effluent. There was observed about 79% of colour removal in addition to good reduction of C.O.D. (51%). See Table-II.

When coagulant (lime) alone was used resulted in the formation of slimy sludge with poor settling properties which makes reclamation of sludge difficult. Therefore, it was essential to use flocculator to improve sludge settling rate. In view of chemical value recovery from effluent sludge the calcium carbonate (lime mud from lime recovery section) was chosen as flocculating aid to settle precipitated coloured organo-calcium salts. It was interesting to observed that the increased improvement in the colour of the effluent when calcium carbonate was used along with lime. Otherwise one would not have not higher decolourisation with lime alone. The combination of 1000 mg of lime and 30,000 mg. of Calcium carbonate (50% dry lime mud) per litre of effluent found to be suitable, by which it was possible to achieve colour

TABLE—I

Description	Colour Pt. Co.	Total Solids mg/l.	TSS mg/l.	COD mg/l.	BOD mg/l.	Total flow (M <sup>3</sup> )	pH	Total Load per day in tonnes	
								COD	BOD
pH-Liquor + pH-Wash	6000	35000	700	60000	30000	1600	3.0	96.0	48.0
Brown Wash	6500	1500	200	2000	300	7000	9.5	17.5	2.1
Acid Bleach	700	1900	150	600	150	6500	3.2	3.9	0.97
Bleach 1st Alkali Extraction	4500	2700	160	1500	185	2500	10.0	3.7	0.46
Alkali Bleach Excluding 1st alkali extraction	800	2000	145	700	160	5500	9.5	3.85	0.88
Evaporator	3000	1400	250	800	225	2500	10.0	2.0	0.56
White water	45	575	250	60	25	1000	4.0	0.06	0.025
Causticizing	150	3800	3000	125	20	2000	9.0	0.25	0.04
Paper Plant	75	1500	1000	150	80	1500	4.0	0.22	0.12
Chipper House	65	250	180	60	10	2400	7.0	0.144	0.02
Total	—	—	—	—	—	31600	—	128	52.2

Note :—Pulping process deviation leads to effluent characteristic variation.

TABLE—II

Source	Before Treatment			After Treatment with Lime 1000 mg + 30,000 mg. Lime mud			Sludge volume in ml.			After Treating with 100 mg/l. Chlorine		
	Colour Pt. Co.	COD mg/l.	pH	Colour Pt. Co.	COD mg/l.	pH	60 Min.	120 Min.	180 Min.	Colour Pt. Co.	COD mg/l.	pH
(% Reduction)										( % with respect to original value)		
1. Washing back water	6500	2000	9.5	1350 (79)	910 (54)	11.4	125	100	79	—	—	—
2. Bleaching 1st Alkali Extraction	4500	1400	10	1020 (77)	650 (55)	11.8	„	„	„	—	—	—
3. Evaporators	3000	800	10	750 (75)	375 (53)	11.7	„	„	„	—	—	—
4. A mixture of 1 + 2 + 3	5000	1500	9.5	1050 (79)	735 (51)	11.6	124	99	78	550 (89)	755 (50)	8.7

Note :— (i) In all cases 1000 mg. of lime and 30,000 mg. of lime mud (50% dry) was used.

(ii) During these experiments mill open system was operating.  
(Washing backwater was let out as effluent).

TABLE—III

Source	Before treatment		pH	After treatment		pH	After chlorine treatment		pH
	Colour	COD		Colour	COD		Colour	COD	
	Pt.co.	mg/l		Pt.co.	mg/l		Pt.co.	mg/l	
				(% reduction)			(% reduction with respect to original value).		
1. Bleaching 1st Alkali extraction	7700	1529	10.2	900 (88)	529 (65)	11.8	—	—	—
2. A mixture of 1 + Evaporator Effluent	6600	1350	10.0	850 (87)	510 (62)	11.7	450 (93)	535 (60)	9.4

Note:— (i) Experiments were conducted when mill was operating close system.  
(Washing backwater was recycled in the system).

(ii) In these experiments fresh lime and (50% dry) lime mud was used.

(iii) Small quantity of Chlorine was also charged.

removal to the tune of 79% along with 51% COD reduction when the mill was running open system (refer Table-II).

During close system of mill operation coloured process water from bleaching first alkali extraction and recovery section need be treated as washing back water would be recycled in the process. After conducting several trials appropriate quantity of lime to be added was found out and lime mud quantity was decided so as to obtain solid content in the effluent sludge above 20% to facilitate improved filtration to attain finally above 50% dry content. Colour and COD reduction could be achieved to the tune of 87 and 62 percent respectively (Table-II and III).

#### CHLORINATION OF LIME TREATED EFFLUENT

After the lime treatment, the clarified effluent was allowed to react with small quantity of Chlorine. In about 30 minutes there was observed significant improvement in colour whereas there was no further reduction in COD. The average colour reduction was in the range of 89-93% (Tables-II and III).

In exact mode of Chlorine bleaching in this case is not understood. However, it has been assumed here that the calcium hypochlorite is generated in site. The probable mechanism operating would be, in the 1st stage, Chlorine readily reacts with the dissolved calcium hydroxide in the effluent given rise to calcium hypochlorite which subsequently acts as a bleaching agent.

#### CALCINING OF EFFLUENT SLUDGE

The effluent sludge (50% dryness) obtained from

both trials (open and close systems) was subjected to calcining to know the burning properties. For the purpose of comparison a representative sample of fresh lime mud was also calcined along with effluent sludge. It has been observed that the lime obtained from the effluent sludge had better appearance, and also higher available calcium oxide than the lime obtained from fresh lime mud under the same experimental conditions. A typical experimental results are recorded in Table-IV.

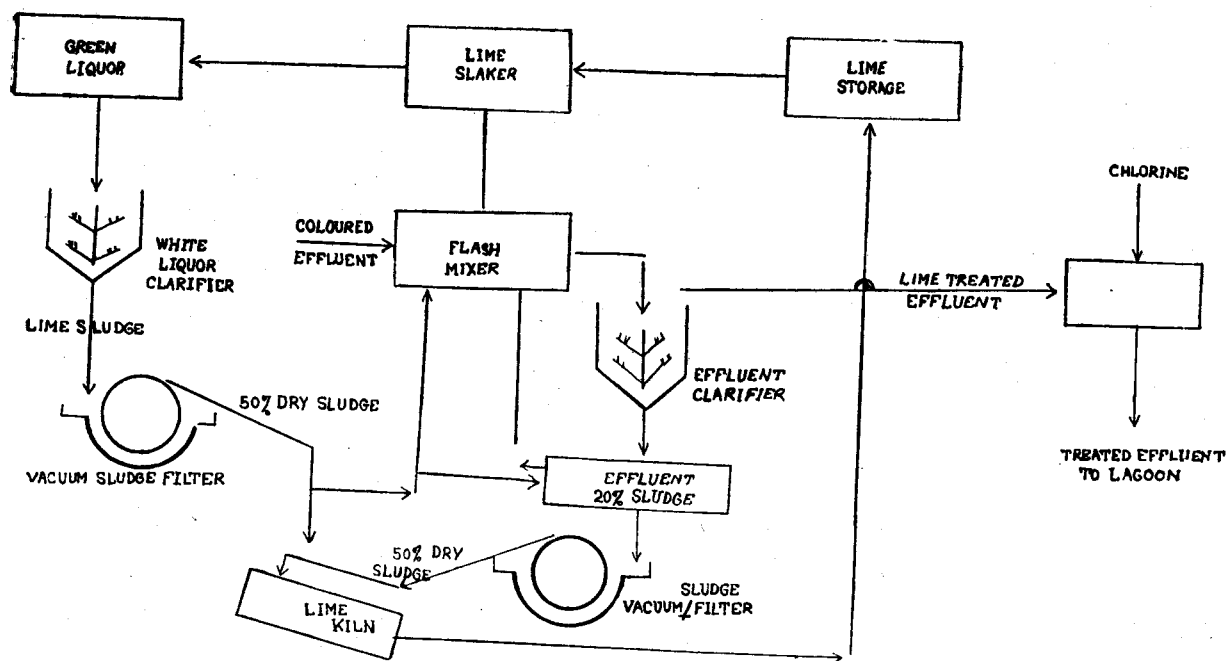
TABLE—IV

Description	Weight of sludge taken	Weight of lime obtained on calcining
Representative sample of fresh lime mud	50 g. (O.D.)	30 g. (white lumps)
Available lime	—	72.8%
Acid Insolubles	—	10.9%
Effluent lime sludge, obtained during treatment	50 g. (O.D.)	28 g. (white powder)
Available lime	—	77.2%
Acid Insolubles	—	9.85%

Note :—Calcining temperature 900°C (3 hrs)

#### CAUSTICIZATION USING LIME OBTAINED FROM EFFLUENT SLUDGE

To study the behaviour of lime obtained from effluent sludge (Table-IV) single Causticizing experiment was performed.



Flow Diagram of Decolourisation of Dissolving Pulp Mill Coloured Effluent.

Green liquor (250 ml) was treated with effluent lime (25 g.) at 95 °C with constant stirring. The stirring was continued for a further period of 1.5 hrs. maintaining 95-100 °C. The reaction mixture was allowed to cool and the sludge thus settled was separated by decantation. Care was taken to avoid change on the volume of green liquor during experiment. The analysis of Green and White liquors are recorded in the following Table-V which shows that the lime obtained from the effluent sludge gives quite satisfactory results.

TABLE—V

Description	Green Liquor	White Liquor
TTA g.p.l.	126.14	126.48
A.A.	50.36	110.98
NaOH	29.28	88.66
Na <sub>2</sub> S	21.08	22.32
Na <sub>2</sub> CO <sub>3</sub>	75.78	15.5
Causticity	27.80	85.1
Sulphidity	41.86	20.1

### CONCLUSION

This process can hopefully be adopted successfully to treat pulp mill coloured effluent to an acceptable standard while providing no sludge handling problems.

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